Shimadzu IRAffinity-1

User Guide and Tutorial for Taking IR Measurements
in the Reynolds Research Group
2nd Edition: April 2012

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Shimadzu IRAffinity-1 User's Manual

1. Introduction

1.1. Basic Principles of Infrared Spectroscopy

Infrared (IR) spectroscopy is one of the most common techniques used in organic chemistry for the identification of structural characteristics of various substances or mixtures thereof. When an organic compound is subjected to electromagnetic radiation in the infrared frequency range (780 nm to 1000 μm, or 13,000 to 10 cm^{-1}), the absorbed resonant frequencies give the molecules enough energy to allow their bonds to stretch, bend or rotate more actively. The resonant frequency depends on the strength of the bond, which in turn depends on the atoms connected by the bond, the type of bond involved, and to a certain extent, the environment around each bond.

Specifically, the mid-infrared range (4000 to 400 cm^{-1}) of frequencies is the most useful in organic chemistry. Most functional groups have characteristic absorptions in this frequency range, and these characteristic absorptions are used to identify what functional groups are present in a sample. The characteristic absorptions of some common functional groups can be found in section _____.

Comment [BR1]: I've moved this to the appendix

1.2.

2. The Shimadzu IRAffinity-1 Spectrometer

The Shimadzu IRAffinity-1 Spectrometer, like most FTIR spectrometers, makes use of a Michelson interferometer with a movable mirror. A schematic diagram of this instrument is shown in Figure 1.

The IRAffinity-1 uses a high-energy long life ceramic light source (1), which sends light to a spherical mirror (2). The beam is then converged at the aperture (3), and is sent to the collimator (4) to make parallel beams that are sent to the interferometer.

The beam splitter (6,7) divides the light beam to the fixed mirror (8) and the moving mirror (9). When the distance between the beam splitter and the fixed mirror equals the distance between the moving mirror and the beam splitter, the beams are in phase, and interfere constructively. When the moving mirror is displaced by ¼ of the wavelength of

the beam from the source, the two beams will be out of phase and will interfere destructively. This optical path difference is measured very accurately via a He-Ne laser.

In the IRAffinity-1, the beam splitter is made of a potassium bromide substrate on which germanium is evaporated. This beam splitter is very easily damaged by moisture, and as such, it is protected with a moisture resistant coating. Furthermore, the instrument is equipped with a dehumidifier. Nevertheless, care must be taken to avoid moisture building up in the instrument.

These two beams are then reflected by two flat mirrors (10, and 11), and are converged at another mirror (13). The resulting parallel interfered beam then goes through the sample compartment. Thereafter, the beam goes through another converging mirror (14) and then to the detector (15). For this instrument, the detector is a DLATGS (deuterated L-alanine triglycene sulfate) pyroelectric detector, which has a high sensitivity and does not require cooling.

Figure 1.

As explained above, the instrument is sensitive to humidity, and, therefore, it has been equipped with a ROSAHL dehumidifier, which keeps the instrument at low humidity. However, this unit must constantly be connected to a power supply to keep the dehumidifier running.

3. How to Use the IRAffinity-1 FTIR system and the IRSolution software

3.1. Sampling Accessory Selection and Installation

Comment [BR2]: I've moved the table to the appendix as well

3.1.1. MIRacle Single Reflection Horizontal ATR Accessory

For most types of samples, such as oils, powders, crystals, free-standing polymer films, pastes, and intractable materials, the PIKE Technologies MIRacle sampling accessory is suitable. This accessory allows for single- or multi-reflection attenuated total reflectance (ATR) and specular reflectance measurements. In the common configuration, the MIRacle accessory is a single-reflection ATR sampling accessory. This is used for most samples, as it allows characterization of thick or strongly absorbing samples without any need for sample preparation.

To install this accessory, place the entire accessory into the sample compartment of the spectrometer, with the PIKE label facing outward. Align the base plate of the accessory on the spectrometer with the use of the pins on the accessory, and the corresponding holes on the spectrometer. Fasten the accessory using the captive screw located on the left side of the accessory base plate, and tighten by hand.

Generally, the accessory will not require any alignment once installed. If, however, there is a need to realign or fine-tune the accessory, inform the person-in-charge. The IRSolution software, may, however, run an autoadjustment, which will be discussed later.

3.1.2. 30Spec 30 Degree Specular Reflectance Accessory

The Specular Reflectance accessory is most commonly used for thin films of samples that do not transmit infrared light. (to be continued)

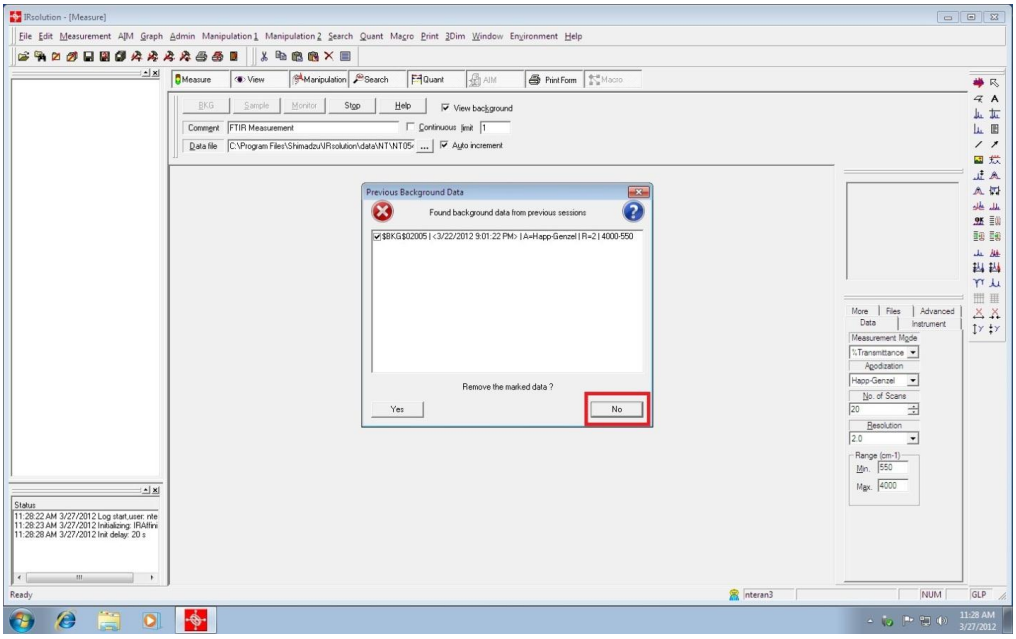
3.1.3. EasiDiff Diffuse Reflectance Accessory

(to be continued)

3.2. Starting up the FTIR system

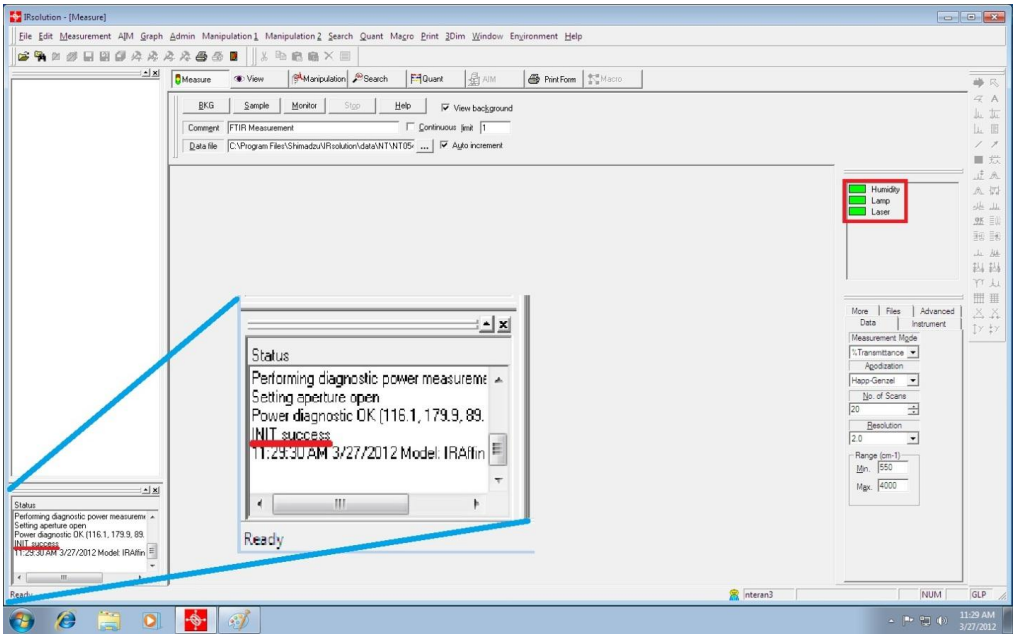
Turn on the spectrometer by pressing the power switch (remember: the instrument should always be connected to a power source). Turn on the computer and monitor attached and log into your GT account. Once Windows has completed the PC start-up process, double-click on the [*IRSolution*] icon on the desktop to start the FTIR software.

When available, the instrument stores the background spectrum obtained from the latest use. Thus, usually, you will see the following message upon opening the IRSolution software:

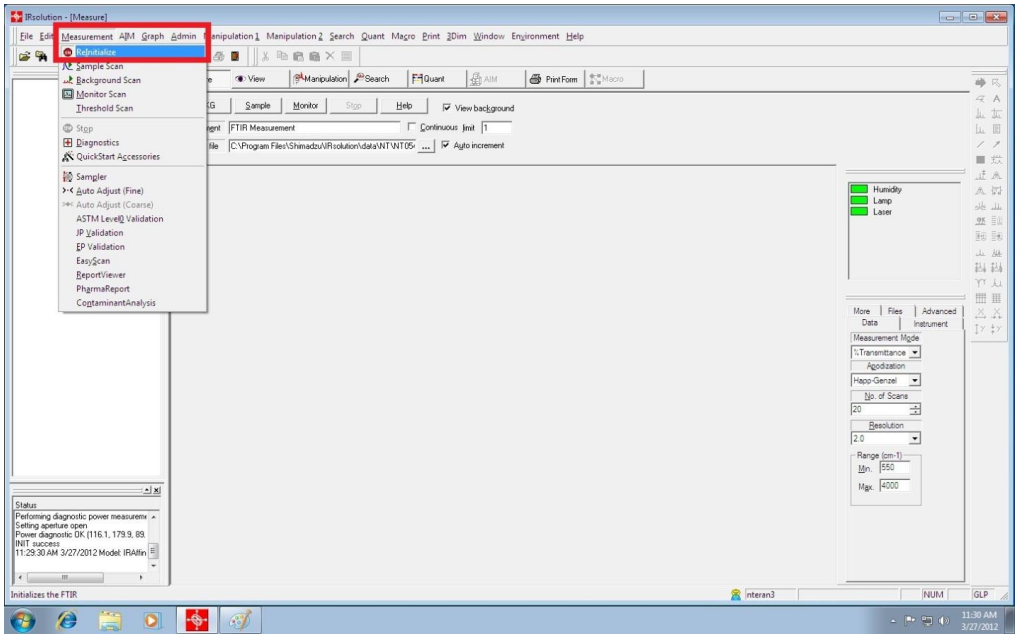


Since it is best to obtain a background spectrum just before obtaining your sample spectrum, it is advisable to click [*No*] on the above message window.

The instrument has been preconfigured to initialize as soon as the IRSolution software starts. Initialization may be verified on the *Status* window displayed on the bottom left corner of the IRSolution window. Upon successful initialization, the *Status* window should reflect this, as shown below.

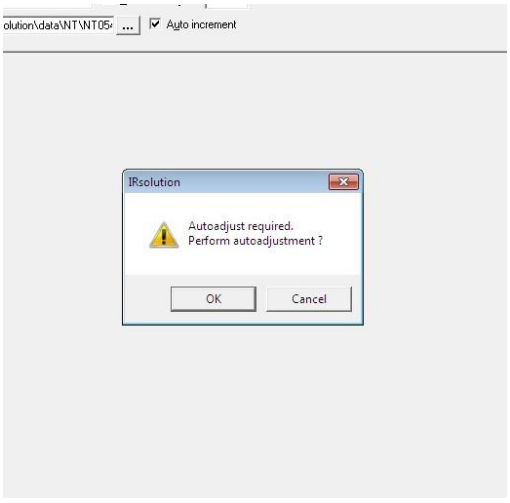


However, should this not occur, you can manually initialize the instrument by clicking the *Measurement* menu and then choosing *ReInitialize*.



Again, the *Status* window should display the *INIT success* message upon a successful initialization.

If a sampling accessory is in place, the spectrometer may need to perform an automatic adjustment, which resets certain parameters to accommodate the change in the optical path. The following dialog box will appear:



Click [*OK*]. The instrument will take a few minutes to perform the auto-adjustment, and a progress bar will be displayed.

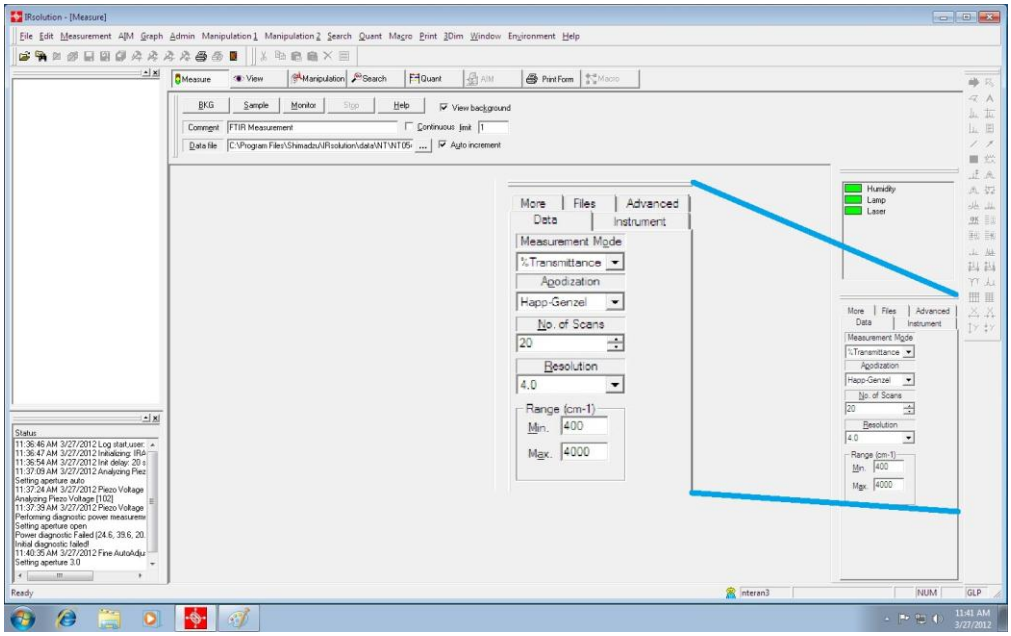
Check to make sure that all messages shown for a successful initialization are present (see above).

3.2.1. Trouble shooting initialization errors

3.3. Data acquisition

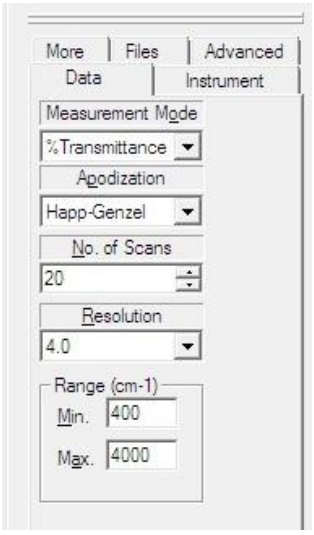
3.3.1. Setting the Scanning Parameters

Normally, the Scan Parameters need not be changed, but if necessary, it can be found while on the *Measure* tab, on the bottom right corner of the screen. It consists of five tabs, namely: *Data*, *Instrument*, *More*, *Files*, and *Advanced*.



3.3.1.1. Data Tab

The *Data* tab gives five parameters to set:



3.3.1.1.1. Measurement Mode

In measurement mode, select whether the measured spectra are to be displayed in absorbance or transmittance modes. Usually, IR spectra are displayed in transmittance mode. However, for purposes of quantitation, it is more appropriate to display the spectra in absorbance mode.

Comment [E3]: You mean "quantification"?

This mode also gives the option of obtaining a *Power* spectrum. (WHY??? WHAT FOR???)

3.3.1.1.2. Apodization

The Apodization function selected is a tapering function that smoothes the interferogram obtained by the instrument to zero at the ends of the sampled region. It affects the resolution and the signal-to-noise ratio (S/N ratio) of the spectra, so proper selection is necessary. Under most common measurements, the *Happ-Genzel* is selected. For measurements of high resolution, *Box-Car* may be selected. For small samples requiring high S/N ratio, *SqrTriangle* may be selected.

3.3.1.1.3. No. of Scans

The number of scans (1 to 4000) affects the S/N ratio of the obtained spectra. For a better S/N ratio, a larger number of scans can be selected at the expense of a longer measurement time. Normally, the parameter is set to collect 20 scans.

3.3.1.1.4. Resolution

For solids and liquids, a resolution of 4 or 8 cm^{-1} is sufficient. For gas samples, some minute absorption peaks may be neglected at these resolutions. Therefore, a resolution of 0.5 cm^{-1} is usually desired. Higher resolutions lead to longer measurement times and poorer S/N ratios, and therefore, setting to higher resolutions than necessary is not recommended.

3.3.1.1.5. Range

The Range set depends on the desired measurement and the detector. Most commonly for this instrument, a minimum of 400 and a maximum of 4000 cm^{-1} are set.

3.3.1.2. Instrument Tab

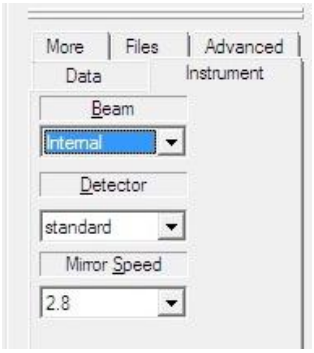
The Instrument tab parameters are only changed when the instrument is coupled with an external IR microscope or a different sampling kit from the standard sample compartment and the *MIR*acle sampling accessory. Changing these parameters will be discussed under the section for Sampling Accessories.

The normal settings are:

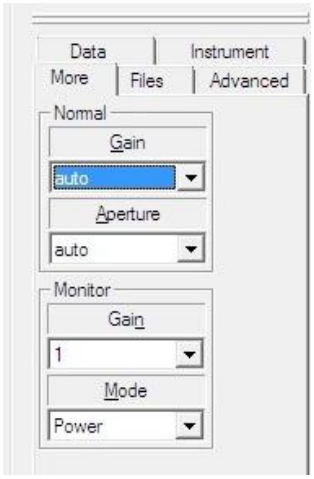
Beam: *Tab*

Detector: *Standard*

Mirror Speed: *2.8*

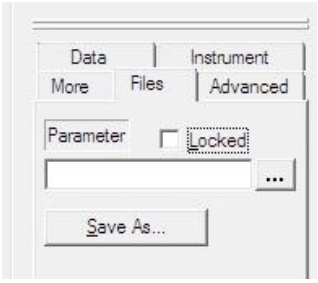


3.3.1.3. More Tab

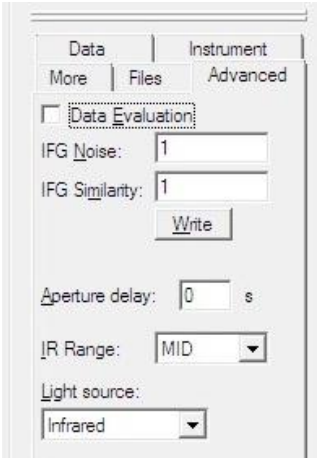


3.3.1.4. Files Tab

The *Files* tab is used to set the saving parameters, such as the destination directory and the file name. To set, click the [*Save As*...] button. To load saved parameters, click the [...] button.



3.3.1.5. Advanced Tab



3.3.2. Obtaining a Background Spectrum

Make sure that the particular sampling accessory to be used with your sample is in place in the sample compartment. Without any sample loaded onto the accessory, take a background measurement. While on the *Measure* tab of the main window, click the [*BKG*] button. A dialog box will appear requiring you to verify that no sample is in the path of the beam:

(screen shot)

Confirm that this is so, and click the [*OK*] button. Background measurement will commence and the spectra scanned will be displayed under the *View* tab while it is being updated in real-time, while the progress of background measurement will be displayed on the status bar on the lower left corner of the screen.

(screen shot)

A normal background spectrum will look like the one shown above for measurements taken in air. If the background spectrum you obtain differs from this, check to make sure there is no sample on the sample holder, or that the crystal plate for the MIRacle accessory is thoroughly cleaned (refer to the cleaning section if necessary).

3.3.3. Sample Preparation and Sampling Procedure

3.3.3.1. MIRacle Single Reflection Horizontal ATR Accessory

As noted above, no sample preparation is required for the MIRacle accessory, but make sure that the sample is at room temperature. Begin by making sure that the swiveling arm of the pressure clamp is detached or directed away from the sample plate, and raised at a sufficient height so that it is elevated a good distance from the sample plate surface.

(figure)

Once a background spectrum has been obtained (see above for instructions), load enough sample to fully cover the 1.8mm sampling area in the center of the crystal plate. For oils, data collection can be done without using the pressure clamp. For solids and soft pliable films for which an intimate contact between the sample and the crystal surface is not readily ensured, use the pressure clamp. If the pressure clamp is not already mounted on the accessory, mount it to the backside of the accessory using the two alignment dowel pins on top of the MIRacle accessory base and using a flathead screwdriver, fasten the two captive screws on the clamp frame.

Swivel the arm of the pressure clamp so that the tip is directly above the crystal plate (a locking mechanism with an audible click prevents swinging the arm farther than necessary). Lower the pressure tip so that it is in contact with the sample by rotating the large black control knob on the clamp column until an audible click is heard. This control knob features a ratchet-type clutch mechanism that protects the crystal from damage from over-pressuring by controlling the maximum allowable pressure applied on the crystal. Proceed with data collection.

3.3.3.2. 30Spec 30 Degree Specular Reflectance Accessory

The Specular Reflectance accessory is most commonly used for thin films of samples that do not transmit infrared light. (to be continued)

3.3.3.3. EasiDiff Diffuse Reflectance Accessory

(to be continued)

3.4. Data collection

Once the sample has been loaded onto the proper sample holder, click the Measure tab and then click the [Sample] button. Sample spectra will be collected and once again the progress in measurement will be displayed in the status bar, while the real-time window will display the sample spectrum in transmittance mode.

While spectra is being collected, the measurement can be paused and restarted. Click the [Stop] button to pause. The following dialog box will appear:

(screen shot)

To stop the measurement and display the spectrum (up to the number of scans obtained), click the [Stop] button on the dialog box. To stop measurement and abandon the data acquired, click the [Abort] button. To resume measurement, click the [Cancel] button.

Once the measurement is completed, the main window will switch to the View tab. The spectra will be displayed in two windows, with the upper window being the full view of the spectra, called the "Overview" window, while the lower window being the Zooming window.

3.5. Spectral Manipulation

3.6. Data processing

3.7. Data templates and printing

3.8. Library searching

3.9. Cleaning the Sampling Accessory

4. Common applications for Reynolds Group

4.1.

5. Special applications

5.1. Attenuated Total Reflectance

5.2. Specular reflectance

5.3. Diffuse reflectance

5.4.

6. Transferring data and preparation of spectra using other graphing software

7. Care and maintenance of the instrument

7.1. Protection against humidity

7.2. Protection against vibrations

8. General Trouble shooting

9. Appendix

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9.1. Diagram of the sampling accessories and their specific applications

Sample		Analytical form and analytical condition	Accessory
Solids	Rubbers	Total reflectance method	ATR-8000A, etc.
			MIRacle
			Dura sampler
		Liquid film method	Demountable cell
	Powders	Total reflectance method	ATR-8000A, etc.
		KBr pellet method	KBr die + hydraulic press + vacuum pump
		Nujol method	Demountable cell

		Diffuse reflectance method		DRS-8000A（mix with KBr powder）
	Paper, cloth, yarns	Total reflectance method		ATR-8000A, etc
				MIRacle
				Dura sampler
		Transmission method		Film holder（Use a grid polarizer for study of molecular orientation）
	Film, plastics	Total reflectance method		ATR-8000A, etc
				MIRacle
				Dura sampler
		Transmission method		Film holder（Use a grid polarizer for study of molecular orientation）
		Film method		Demountable cell（Evaporate the solvent to obtain the film）
		Grind		SiC sampler
	Coating films on metals	Thicker than 1μm	Total reflectance method	ATR-8000A（Measurement to a depth of 1/5 of the wavelength with a KRS-5 prism and to 1/10 with a Ge prism）
			Specular reflectance method	SRM-8000A
		Thinner than 1μm	Reflection absorption spectrometry	RAS-8000A（Use of a grid polarizer enhances sensitivity about two times）
		Mix with KBr powder	KBr pellet method	KBr die + hydraulic press + vacuum pump

		Diffuse reflectance method		DRS-8000A
	Coating films on resins	Total reflectance method		ATR-8000A（Measurement to a depth of 1/5 of the wavelength with a KRS-5 prism and to 1/10 with a Ge prism）
		Specular reflectance method		SRM-8000A（Convert a reflection spectrum into an absorption spectrum by the Kramers-Kronig method）
	Semiconductors	Direct measurement		Film holder
Liquids	Oil content measurement	Measures mineral oils only		Quartz cell
		Also measures animal/plant oils		CaF2 cell
	Nonvolatile organic solvents	Liquid film method		Demountable cell
	Volatile organic solvents	Solution method		Fixed thickness cell, sealed liquid cell
		Rapid measurement	Liquid film method	Demountable cell
	Aqueous solutions	Above 10% in concentration	Liquid film method	Demountable cell with KRS-5
		Below 10% in concentration	ATR method	Horizontal type or cylinder internal reflection type ATR attachment
	Extract solutions	Difference spectrometry	Solution method	Fixed thickness cell
		Evaporate solvent	Diffuse reflectance method	DRS-8000A（The sample solution is supplied dropwise on KBr powder and measured after evaporating the solvent）

Gases	% level	5cm/10cm gas cell
	ppm level	Long-path gas cell（Detection limit is 0.1～1ppm with 10m optical path）
Micro/trace samples	Liquids（μL level）	Micro cell
	Solids（μ level）	AIM-8800（Applicable to transmission, reflection, and ATR methods

Source: http://www.shimadzu.com/an/spectro/ftir/accessory/guide.html

9.2. ~~Table 1.~~ Characteristic Infrared Absorptions of Common Functional Groups

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Bond	Type of bond	Specific type of bond	Absorption peak	Appearance
C—H	alkyl	methyl	1260 cm^{-1}	strong
			1380 cm^{-1}	weak
			2870 cm^{-1}	medium to strong
			2960 cm^{-1}	medium to strong
		methylene	1470 cm^{-1}	strong
			2850 cm^{-1}	medium to strong
			2925 cm^{-1}	medium to strong
		methine	2890 cm^{-1}	weak
	vinyl	C═CH_2	900 cm^{-1}	strong
			2975 cm^{-1}	medium
			3080 cm^{-1}	medium
		C═CH	3020 cm^{-1}	medium
		monosubstituted alkenes	900 cm^{-1}	strong
			990 cm^{-1}	strong
		cis-disubstituted alkenes	670–700 cm^{-1}	strong
		trans-disubstituted alkenes	965 cm^{-1}	strong

		trisubstituted alkenes	800–840 cm^{-1}	strong to medium
	aromatic	benzene/sub. benzene	3070 cm^{-1}	weak
		monosubstituted benzene	700–750 cm^{-1}	strong
			690–710 cm^{-1}	strong
		ortho-disub. benzene	750 cm^{-1}	strong
		meta-disub. benzene	750–800 cm^{-1}	strong
			860–900 cm^{-1}	strong
		para-disub. benzene	800–860 cm^{-1}	strong
	alkynes	any	3300 cm^{-1}	medium
	aldehydes	any	2720 cm^{-1}	medium
			2820 cm^{-1}	
C─C	acyclic C─C	monosub. alkenes	1645 cm^{-1}	medium
		1,1-disub. alkenes	1655 cm^{-1}	medium
		cis-1,2-disub. alkenes	1660 cm^{-1}	medium
		trans-1,2-disub. alkenes	1675 cm^{-1}	medium
		trisub., tetrasub. alkenes	1670 cm^{-1}	weak
	conjugated C─C	dienes	1600 cm^{-1}	strong
			1650 cm^{-1}	strong
	with benzene ring		1625 cm^{-1}	strong
	with C═O		1600 cm^{-1}	strong
	C═C (both sp^2)	any	1640–1680 cm^{-1}	medium
	aromatic C═C	any	1450 cm^{-1}	weak to strong (usually 3 or 4)
			1500 cm^{-1}	
			1580 cm^{-1}	
			1600 cm^{-1}	
	C≡C	terminal alkynes	2100–2140 cm^{-1}	weak
		disubst. alkynes	2190–2260 cm^{-1}	very weak (often indisinguishable)
C═O	aldehyde/ketone	saturated aliph./cyclic 6-membered	1720 cm^{-1}	

		α,β-unsaturated	1685 cm^{-1}	
		aromatic ketones	1685 cm^{-1}	
		cyclic 5-membered	1750 cm^{-1}	
		cyclic 4-membered	1775 cm^{-1}	
		aldehydes	1725 cm^{-1}	influence of conjugation (as with ketones)
	carboxylic acids/derivates	saturated carboxylic acids	1710 cm^{-1}	
		unsat./aromatic carb. acids	1680–1690 cm^{-1}	
		esters and lactones	1735 cm^{-1}	influenced by conjugation and ring size (as with ketones)
		anhydrides	1760 cm^{-1}	
			1820 cm^{-1}	
		acyl halides	1800 cm^{-1}	
		amides	1650 cm^{-1}	associated amides
		carboxylates (salts)	1550–1610 cm^{-1}	
		amino acid zwitterions	1550–1610 cm^{-1}	
O─H	alcohols, phenols	low concentration	3610–3670 cm^{-1}	
		high concentration	3200–3400 cm^{-1}	broad
	carboxylic acids	low concentration	3500–3560 cm^{-1}	
		high concentration	3000 cm^{-1}	broad
N─H	primary amines	any	3400–3500 cm^{-1}	strong
			1560–1640 cm^{-1}	strong
	secondary amines	any	>3000 cm^{-1}	weak to medium
	ammonium ions	any	2400–3200 cm^{-1}	multiple broad peaks

C─O	alcohols	primary	1040–1060 cm^{-1}	strong, broad
		secondary	~1100 cm^{-1}	strong
		tertiary	1150–1200 cm^{-1}	medium
	phenols	any	1200 cm^{-1}	
	ethers	aliphatic	1120 cm^{-1}	
		aromatic	1220–1260 cm^{-1}	
	carboxylic acids	any	1250–1300 cm^{-1}	
	esters	any	1100–1300 cm^{-1}	two bands (distinct from ketones, which do not possess a C─O bond)
C─N	aliphatic amines	any	1020–1220 cm^{-1}	often overlapped
	C═N	any	1615–1700 cm^{-1}	similar conjugation effects to C═O
	C≡N (nitriles)	unconjugated	2250 cm^{-1}	medium
		conjugated	2230 cm^{-1}	medium
	R─N─C (isocyanides)	any	2165–2110 cm^{-1}	
	R─N═C═S	any	2140–1990 cm^{-1}	
C─X	fluoroalkanes	ordinary	1000–1100 cm^{-1}	
		trifluromethyl	1100–1200 cm^{-1}	two strong, broad bands
	chloroalkanes	any	540–760 cm^{-1}	weak to medium
	bromoalkanes	any	500–600 cm^{-1}	medium to strong
	iodoalkanes	any	500 cm^{-1}	medium to strong
N─O	nitro compounds	aliphatic	1540 cm^{-1}	stronger
			1380 cm^{-1}	weaker

		aromatic	1520, 1350 cm^{-1}	lower if conjugated

Source: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table

(update with information from other reliable sources)

Bond Type	**Functional Group**	**Absorption Range (cm^{-1})**	**Assignment**	**Intensity**
C – H				
alkyl	methyl	1260		strong
		1380		weak
		2870		medium to strong
		2960		medium to strong
	methylene	1470		strong
		2850		medium to strong
		2925		medium to strong
	methine	2890		weak
vinyl	$C=CH_2$	900		
		2975		
		3080		
	C=CH	3020		
	monosubstituted alkenes	900 990		
	cis-disubstituted alkenes	670-700 965		
	trans-disubstituted alkenes	800-840		
aromatic	trisubstituted alkenes			
	benzene/substituted benzene			
alkyne				
aldehyde	monosubstituted benzene			
	ortho-disubstituted			

	benzene meta-disubstituted benzene			
C – C acyclic conjugated C-C C=C benzene C=C	Alkenes			
	Alkynes			
	Alkyl Halides			
	Alcohols			
	Arenes			
	Amines			
	Aldehydes and Ketones			
	Carboxylic Acids and Derivatives			
	Disulfides			
	Esters			
	Nitriles			
	Isocyanates, Isothiocyanates, Diimides, Azides, Ketenes			

~~8. General Trouble shooting~~